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CHALCOPYRITE MAGNETIC SEMICONDUCTORS: AN AB-INITIO STUDY OF THEIR STRUCTURAL, ELECTRONIC AND MAGNETIC PROPERTIES

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ABSTRACT

Stimulated by recent experimental observations of room-temperature ferromagnetism of $\text{Mn}_x\text{Cd}_{1-x}\text{GeP}_2$, we investigate the structural, electronic and magnetic properties of these systems as a function of Mn concentration by means of first-principles density-functional-theory-based codes. Moreover, we investigate the effect of the anion substitution (P vs As) in Mn-rich chalcopyrites. Our calculations indicate that the antiferromagnetic alignment is the most stable ordering for all the systems studied, at variance with that experimentally reported. Moreover, we find that there is a slight reduction of the total magnetic moment per Mn atom from $\sim 5 \mu_B$ in all the Cd-rich P-based chalcopyrites to $\sim 4 \mu_B$ in the Mn rich MnGeP_2 and MnGeAs_2 systems.

INTRODUCTION AND COMPUTATIONAL DETAILS

A great effort is being devoted to explore new, advanced magnetic semiconductors for spintronics applications[1], based on crystal structures that transcend the limitations (defect formation and too low operating temperatures) of the magnetic zinc-blende systems explored so far (*e.g.* $\text{Mn}_x\text{Ga}_{1-x}\text{As}$). Within this framework, the chalcopyrites seem to be good candidates; the expected advantage of these systems is that Mn can readily substitute for the type-II cations, as has been demonstrated for $\text{II}_{1-x}\text{Mn}_x\text{VI}$ alloys with x up to 1.0 without defect formation, due to the natural tendency of Mn to adopt a +2 valence state.

Recently, Medvedkin *et al.* [2] deposited a Mn overlayer in vacuum on the surface region of a CdGeP_2 crystal, followed by a solid phase reaction at elevated temperatures. A relevant finding of Medvedkin *et al.* is the room temperature ferromagnetism in highly doped $\text{Mn}_x\text{Cd}_{1-x}\text{GeP}_2$ - which constitutes a tremendous improvement from the T_C of 110 K found in $\text{Mn}_x\text{Ga}_{1-x}\text{As}$ at $x = 5.3$ %. Moreover, their photoluminescence spectrum at 20 K shows a peak around 3.2 eV, from which they proposed a Mn induced enhancement of the energy gap of CdGeP_2 ($E_g = 1.83$ eV). This is quite different from the III-V alloys, in which Mn is known to reduce the band-gap [7].

In order to understand the magnetic interaction in chalcopyrite semiconductors, we investigated $\text{Mn}_x\text{Cd}_{1-x}\text{GeP}_2$ for various x and MnGe(V)_2 where $V = \text{As, P}$ with the full-potential linearized augmented plane wave (FLAPW)[3] method. This is one of the most accurate *ab-initio* methods, in which there is no artificial shape approximation for the wave functions, charge density and potential. For all atoms, the core and valence states are treated fully- and semi-relativistically (*i.e.* without spin orbit coupling), respectively. The muffin tin

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(MT) radii for Cd, Ge, Mn are set to 2.3 a.u.; 2.0 and 1.8 a.u. are used for As and P, respectively. An energy cut off of 9.0 Ry was employed for the wave function expansion in the interstitial region, whereas a 49 Ry cut-off was used for the charge density and potential.

For all the systems studied, we used the generalized gradient approximation (GGA) functional of Perdew-Burke-Ernzerhof [5] rather than the bare local density approximation (LDA) exchange-correlation functional [6], within density functional theory; the GGA was proved to give better agreement with available experimental structural data for Mn pnictides [8] and is therefore likely to describe more accurately the Mn rich chalcopyrites.

STRUCTURAL DETAILS

Let us first focus on the structural details. Recall that the chalcopyrite differs from the zincblende crystal structure by a doubling of the unit cell along a four fold axis, rendering the system body centered tetragonal. Through total energy calculations, we fully optimized the MnGeAs_2 system, obtaining $a = 5.83$ Å, $c/a = 1.95 \pm 0.05$ and $u \sim 0.25$. The estimated numerical uncertainty on the η value can be ascribed to the very small effect on the total energy due to the tetragonal deformation (*i.e.* $\eta = c/2a \neq 1$) around the η equilibrium value. Our optimized structural values are in good agreement (within 0.5 % on the a lattice constant) with the values predicted by the "conservation of tetrahedral bonds" (CTB) plus $\eta = \eta_{tet}$ theory discussed in Refs. [9]. In our work, Pauling's tetrahedral radii were chosen as 1.48, 1.22, 1.22 and 1.10 Å for Cd, Ge, As and P respectively; the Mn tetrahedral radius, derived from the Mn chalcogenides is 1.41 Å. With these values, we obtained $a = 5.86$ Å and $c/a \sim 1.9$. The good agreement for the As-based chalcopyrite suggests that the "CTB plus $\eta = \eta_{tet}$ " rule may even hold for the similar P-based MnGeP_2 system; we therefore used $a = 5.67$ Å, $c/a = 1.9$. Regarding the MnCdGeP_2 structures [10], we interpolated the lattice constants (a and η) from the experimental values for CdGeP_2 and the "CTB plus $\eta = \eta_{tet}$ " value for MnGeP_2 . This approximation is equivalent to Vegard's law and works well in this system. For instance, it is reported by Medvedkin *et al.* [2] that the lattice constant decreases to 5.7 Å when the Mn concentration becomes greater than Cd, which means x in the range of 50 % to 53 % since the maximum x is 53 % in the experiment. Our interpolated lattice constant for $x=0.5$ is 5.71, which is different from experiment by only 0.4 %. Moreover, in the MnCdGeP_2 systems, we optimized the internal degrees of freedom using both the Dmol³ [4] (*i.e.* density functional theory for molecules and 3-dimensional periodic solids) and the FLAPW codes. More accurate details about the structural properties of MnCdGeP_2 can be found in Ref. [10].

We focused on the dependence of the electronic and magnetic properties in semiconducting chalcopyrites as a function of *i*) the type V anion (*i.e.* P vs As) in Mn rich systems and *ii*) the Mn concentration ($x = 0.25, 0.5$ and 1).

THE MnGeV_2 (V = As, P) SYSTEMS

Let us first discuss the effects due to the anion species by comparing some relevant properties in MnGeP_2 and MnGeAs_2 shown in Table 1. As for the antiferromagnetic (AFM) configurations, we considered a 1x1 chalcopyrite "spin superlattice" along the [001] direction. We find that both the P- and As-based systems largely prefer the AFM alignment, since the AFM is much lower in energy than the ferromagnetic (FM) structures. Let us now consider

Table 1: Comparison of relevant structural and magnetic properties of MnGeP_2 and MnGeAs_2 .

| | MnGeP_2 | | MnGeAs_2 | |
|-----------------------------------|------------------|------|-------------------|------|
| | FM | AFM | FM | AFM |
| Total energy (meV/Mn) | 0 | -160 | 0 | -60 |
| μ_{Mn} (Bohr magn.) | 3.55 | 3.55 | 3.74 | 3.68 |
| Total spin moment/Mn (Bohr magn.) | 4.0 | - | 4.3 | - |
| Mn-anion bond length (Å) | 2.44 | 2.43 | 2.52 | 2.51 |

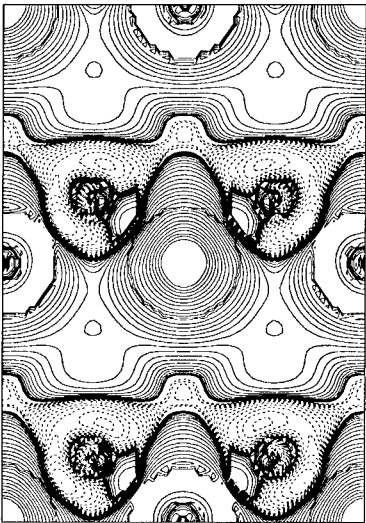


Figure 1: Spin density of ferromagnetic MnGeAs_2 , plotted in the $[110]$ plane. Positive (negative) spin-density is represented by solid (dashed) lines.

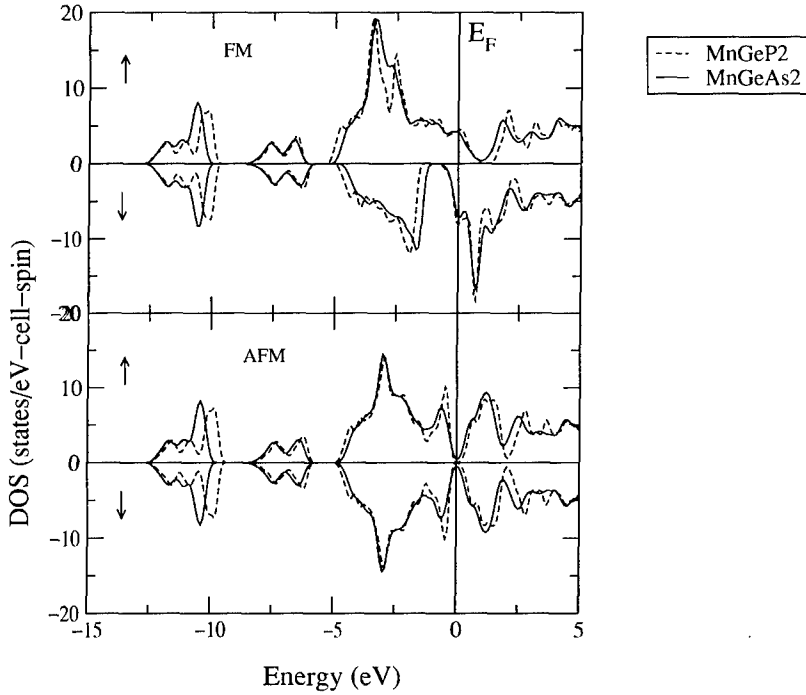


Figure 2: Total density of states of MnGeP₂ (dashed line) and MnGeAs₂ (solid line) for FM (upper panel) and AFM (lower panel) ordering. The zero of the energy scale denotes the Fermi level.

the magnetic moments. In this case, Mn substitutes a type-II cation; we would therefore expect a magnetic moment close to $5.0 \mu_B$. However, note that the local moment relative to the free Mn atom ($\mu_0 = 5 \mu_B$ in the d^5 configuration) is reduced due to the mixing of the unoccupied Mn d^1 bands with the occupied p bands by the $p-d$ hybridization. Note that in both As- and P-based chalcopyrites, the Mn induced FM moment at Ge sites gives positive contributions, while both P and As have a very small induced magnetic moment within the muffin tin sphere. As an example, we plot in Fig. 1 the spin-density in MnGeAs₂ in the $[110]$ plane; it is evident that a negative spin density is present around the As atom, even though there is a positive spin density along the bond.

Let us now discuss the electronic properties of the MnGeAs₂ and MnGeP₂ systems. In Fig. 2 the spin-resolved total density of states for the FM and AFM alignments is reported. Let us first focus on the FM alignment, whose main features are: *i*) around -12 eV we find the hybridized Ge s and, mostly, anion s bands; *ii*) the structure around -7 eV has a similar

Table 2: Relevant structural, electronic and magnetic properties in $\text{Mn}_x\text{Cd}_{1-x}\text{GeP}_2$ for various Mn concentrations. The $x = 0.5$ and 1.0 are 1×1 "spin-superlattices" ordered along the $[001]$ direction, whereas the $x = 0.25$ is ordered along the $[100]$ direction.

| x | 0.25 | | 0.5 | | 1.0 | |
|-----------------------------------|----------|------|----------|------|----------|------|
| | FM | AFM | FM | AFM | FM | AFM |
| MnP bond-length (Å) | 2.43 | 2.43 | 2.44 | 2.43 | 2.44 | 2.43 |
| Total energy (meV/Mn) | 0 | -30 | 0 | -35 | 0 | -160 |
| Total spin moment/Mn (Bohr magn.) | ~ 5 | - | ~ 5 | - | ~ 4 | - |
| Energy gap (eV) | 0.16 | 0.58 | - | 0.49 | - | 0.71 |

origin, with a more marked Ge s character; *iii*) the states at higher energy (*i.e* from -5 eV to +5 eV) have a mixed character. In particular, it is evident that the Mn d^\uparrow states are almost totally occupied (*c.f.* feature peaked at around -3.4 eV in the spin up DOS), whereas the d^\downarrow states are mainly unoccupied and hybridized with the p anion states. (*c.f.* feature going from -0.8 eV, peaked at around 0.5 eV and then up to 5 eV in the spin down DOS). The pronounced feature in the spin-down DOS from -5 eV to -0.8 eV is mainly due to hybridization between Ge p and anion p states. We can estimate a d exchange splitting of about 4 eV. Neither the spin-up nor the spin-down density of states show a gap, therefore resulting in a metallic system; on the other hand, there is a small gap in the spin-down DOS at around -0.8 eV (between the Ge-anion p bands and the Mn d states) which could lead to half-metallicity, possibly by proper modifications in the lattice constants. The main difference between As and P anions stems from the higher hybridization [8] with the Mn d bands, shown by an almost rigid shift of the P (Mn) features towards lower (higher) binding energies with respect to the As case. As for the AFM DOS, we can outline features similar to the FM case. We still find a metallic character, even though a depletion of states is present just around the Fermi level, suggesting a starting gap opening effect. This difference with respect to the FM case is related to the *i*) less evident hybridization between Mn d^\uparrow with anion p^\uparrow states and *ii*) totally unoccupied Mn d^\downarrow antibonding states.

THE $\text{Mn}_x\text{Cd}_{1-x}\text{GeP}_2$ STRUCTURES

Let us now focus on the effect of Mn vs Cd substitution for Cd in the P based chalcopyrites. We report in Table 2 the relevant structural, electronic and magnetic properties of these systems. First of all, note that the AFM alignment is the most stable for all Mn concentrations, although the energy difference between FM and AFM configurations is strongly reduced with respect to the Mn-rich chalcopyrite. These results are not in agreement with the experimental observations[10], that found $\text{Mn}_x\text{Cd}_{1-x}\text{GeP}_2$ to be a room-temperature ferromagnet. The reason for this disagreement is not clear. In our calculations, $\text{Mn}_x\text{Cd}_{1-x}\text{GeP}_2$ is an ideal periodic bulk structure, while in experiment it is a surface doped system with Mn concentration that decays from the surface to the bulk. To resolve this discrepancy, a more thorough and careful experimental characterization is called for. As for the total spin moment, we note that the Mn induced moment on the Cd atom is positive and this is likely to justify the higher total moment for $x = 0.25, 0.5$ than for $x = 1.0$ systems.

Finally, we focus on the energy gap in $\text{Mn}_x\text{Cd}_{1-x}\text{GeP}_2$. Recall that within GGA we obtain strongly underestimated band gaps, with respect to experimental values; for example, we obtain 0.93 eV for the CdGeP_2 crystal, to be compared with the experimental value of 1.83 eV. In the AFM state, the energy gap decreases to 0.49 eV for $x = 0.5$, although it goes up to 0.71 eV for $x = 1.0$. In all cases, the energy gap of $\text{Mn}:\text{CdGeP}_2$ does not exceed that of pure CdGeP_2 . In the FM state, there is no energy gap except for $x = 0.25$. Therefore, the effect of Mn doping on the energy gap in CdGeP_2 is similar to that in $\text{Mn}_x\text{Ga}_{1-x}\text{As}$, where a reduction of the energy gap of the host semiconductor is found. This disagrees with the experimental observation of Medvedkin *et al.*[2], showing an increase of the energy gap upon incorporation in CdGeP_2 .

CONCLUSIONS

The recently reported room temperature ferromagnetism in $\text{Cd}_{1-x}\text{Mn}_x\text{GeP}_2$ was investigated for $x = 1.0$, 0.5 and 0.25 using the FLAPW and DMol codes, within the generalized gradient approximation to the density functional theory. Moreover, we have compared the MnGeAs_2 and MnGeP_2 systems, in terms of structural, electronic and magnetic properties. At variance with recent experimental observations, we find that the total energy of the AFM state is always lower than the corresponding FM state for all the systems studied. The total magnetic moment per Mn atom is close to $5 \mu_B$ for the Cd-rich P-based systems, whereas it is reduced in the Mn-rich P- and As-based chalcopyrites.

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